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EQUILIBRIUM MODEL OF STEAM GASIFICATION OF COAL

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Abstract

Coal gasification is a complex process of parallel-consecutive chemical reactions at high temperature between the organic part of coal matter and the gasifying agent. The following two approaches are applied in modelling the coal gasification process: equilibrium and kinetic. The methods of determining the thermodynamic equilibrium can be divided into two groups: stoichiometric and non-stoichiometric methods. This article presents the equilibrium model of the steam gasification of coal developed for a laboratory experiment (Smoliński 2008, 2011). The scope of this paper includes the development of the concept concerning the division of the reaction system into two zones, where the result of one of the stages constitutes the input data for the subsequent stage. The composition of the gas mixture has been evaluated on the basis of the fundamental physical and chemical rights. The estimated content of the gases in the mixture correlate with the results of the experiment.

Keywords

equilibrium model, gasification, coal

1. INTRODUCTION

Coal gasification is a sequence of thermo-chemical transformations taking place at high temperature between the organic part of coal matter and the gasifying agent, such as: oxygen, steam, air, carbon dioxide. The aim of the process is to produce gas fuel – synthesis gas, which finds wide industrial application, mainly in chemical synthesis. The type of gasifying agent and the process parameters, such as temperature and pressure, mostly affect the energetic properties of the obtained gas (Smoliński 2010; Rauk 1981).

The gasification process is a complex system of parallel-consecutive chemical reactions (Golec, Ilmurzyńska 2008). With regard to chemical calculations, the following two approaches can be distinguished in relation to the problem of modelling the coal gasification process: thermodynamic (equilibrium models) and kinetic (kinetic models).

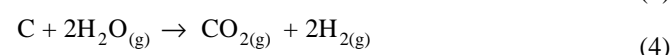
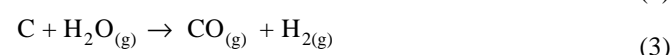
The authors of this article attempt to analyse the hard coal gasification process with steam, based on thermodynamic considerations. The equilibrium models are based on the assumption that the speed of particular chemical and physical-chemical reactions is infinitely high, so that the system remains in thermodynamic equilibrium. The term ‘modelling the gasifying process’ includes the designation of the equilibrium composition of gas formed as a result of the activity of the gasifying agent on the coal sample. The equilibrium composition of the reaction mixture is the one, which would be established, if the reagents remain in direct contact for an infinitely long period of time. Thus, the concentration of

reagents reach limit values at the equilibrium state (Golec, Ilmurzyńska 2008).

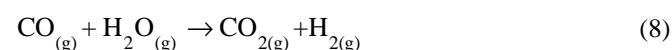
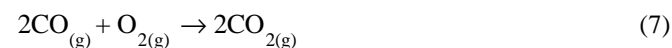
2. SELECTED REACTIONS OF THE GASIFYING PROCESS

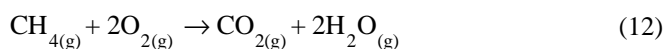
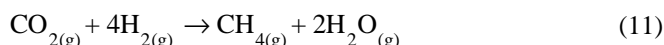
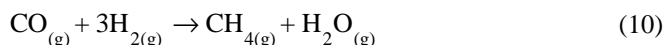
The chemical reactions which are typical for the coal gasification process, assuming that the reaction products do not contain higher organic compounds or higher hydrocarbons (Golec, Ilmurzyńska 2008; Białecka 2008; Tomeczek 1991), are as follows:

- heterogeneous reactions:



- homogenous reactions:





Despite the presence of other components, besides the elemental carbon, in the organic substance of coal, it is assumed that the basic coal gasification reactions can be considered in relation to this element as the substrate. This procedure is justified by a significant fraction of elemental carbon as well as by the need for certain simplifications when dealing with such complex systems (Wasilewski 1980).

3. BALANCING COAL GASIFICATION PROCESSES

The equations of balancing elements in the process are presented below (Kozaczka 1994). The number of particular elements in the fuel (per 1 kmole of fuel) is calculated from the following relation:

$$(C)_{\text{pal}} = \frac{\frac{C}{12}}{\frac{C}{12} + \frac{H}{2} + \frac{O}{32} + \frac{N}{28} + \frac{S}{32} + \frac{W}{18}}, \quad \frac{\text{kmole C}}{\text{kmole of fuel}} \quad (13)$$

$$(H)_{\text{pal}} = \frac{\frac{H}{1} + \frac{W}{9}}{\frac{C}{12} + \frac{H}{2} + \frac{O}{32} + \frac{N}{28} + \frac{S}{32} + \frac{W}{18}}, \quad \frac{\text{kmole H}}{\text{kmole of fuel}} \quad (14)$$

$$(O)_{\text{pal}} = \frac{\frac{O}{16} + \frac{W}{18}}{\frac{C}{12} + \frac{H}{2} + \frac{O}{32} + \frac{N}{28} + \frac{S}{32} + \frac{W}{18}}, \quad \frac{\text{kmole O}}{\text{kmole of fuel}} \quad (15)$$

$$(N)_{\text{pal}} = \frac{\frac{N}{14}}{\frac{C}{12} + \frac{H}{2} + \frac{O}{32} + \frac{N}{28} + \frac{S}{32} + \frac{W}{18}}, \quad \frac{\text{kmole N}}{\text{kmole of fuel}} \quad (16)$$

The number of particular elements in the gasifying agent (per 1 kmole of conversion agent) is calculated from the following relation:

$$(C)_{\text{kon}} = x_{\text{CO}} + x_{\text{CO}_2}, \quad \frac{\text{kmole C}}{\text{kmole of conversion agent}} \quad (17)$$

$$(H)_{\text{kon}} = 2x_{\text{H}_2\text{O}}, \quad \frac{\text{kmole H}}{\text{kmole of conversion agent}} \quad (18)$$

$$(O)_{\text{kon}} = x_{\text{H}_2\text{O}} + 2x_{\text{O}_2} + x_{\text{CO}}, \quad \frac{\text{kmole O}}{\text{kmole of conversion agent}} \quad (19)$$

$$(N)_{\text{kon}} = 2x_{\text{N}_2}, \quad \frac{\text{kmole N}}{\text{kmole of conversion agent}} \quad (20)$$

Assuming that in the process n_{pal} kmoles of fuel react with n_{kon} kmoles of conversion agent, the balance of particular elements in the resultant gas will look as follows:

$$n_{\text{pal}}(C)_{\text{pal}} + n_{\text{kon}}(C)_{\text{kon}} = (C) \quad (21)$$

$$n_{\text{pal}}(H)_{\text{pal}} + n_{\text{kon}}(H)_{\text{kon}} = (H) \quad (22)$$

$$n_{\text{pal}}(O)_{\text{pal}} + n_{\text{kon}}(O)_{\text{kon}} = (O) \quad (23)$$

$$n_{\text{pal}}(N)_{\text{pal}} + n_{\text{kon}}(N)_{\text{kon}} = (N) \quad (24)$$

where:

C, H, O, N, W – the mass fraction of elements in the coal sample, respectively: carbon, hydrogen, oxygen, nitrogen and moisture

$(C)_{\text{pal}}, (H)_{\text{pal}}, (O)_{\text{pal}}, (N)_{\text{pal}}$ – the number of particular elements in the fuel (kmole of element/kmole of fuel)

$(C)_{\text{kon}}, (H)_{\text{kon}}, (O)_{\text{kon}}, (N)_{\text{kon}}$ – the number of particular elements in the conversion agent (kmole of element/kmole of conversion agent)

$(C), (H), (O), (N)$ – the number of particular elements in the synthesis gas, kmole of element $x_{\text{H}_2\text{O}, \text{kon}}, x_{\text{CO}_2, \text{kon}},$

$x_{\text{CO}, \text{kon}}, x_{\text{O}_2, \text{kon}}, x_{\text{N}_2, \text{kon}}$ – the molar fraction of particular gases in the conversion agent, respectively: steam, carbon dioxide, carbon monoxide, oxygen, nitrogen

$n_{\text{pal}}, n_{\text{kon}}$ – the amount of fuel and gasifying agent which have reacted with each other, kmole

4. BASIS OF THE CALCULATION METHOD

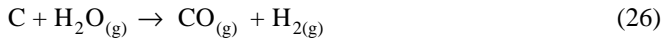
The methods for determining thermodynamic equilibrium can be divided into two groups: stoichiometric and non-stoichiometric methods.

In the non-stoichiometric methods, the input data includes: the initial composition of the reaction mixture, a set of chemical compounds present in the products, expressions determining the thermodynamic potential of each compound, the parameters of the equilibrium state (temperature, pressure). Determination of the equilibrium composition of the mixture in this method consists of finding the number of moles of each of the reagents, which corresponds to the minimum thermodynamic potential. In this method, there is no need to specify the chemical reactions or equilibrium constants (Golec, Ilmurzyńska 2008).

In the stoichiometric methods, the following are assumed as the input data: the initial composition of the reaction mixture, the set of chemical compounds present in the product, the set of chemical reactions, expressions specifying the equilibrium constant of particular reactions, parameters of the equilibrium state (temperature, pressure). The stoichiometric calculation methods differ in the amount of chemical compounds which are taken into consideration and thus, the set of analysed chemical reactions as well as the manner of solving the non-linear system of equations (Kozaczka 1994).

This article refers to the stoichiometric method and in particular, the calculation assumptions proposed by Gumz and Trustel constitute its basis. Gumz extended the calculation scheme proposed by Traustel, by any fuel composition and the pressure higher than the atmospheric pressure (Kozaczka 1994). Therefore, it was assumed that the resultant gas is composed exclusively of the following molecules: carbon dioxide, carbon monoxide, nitrogen, methane, hydrogen, steam. These gases are produced as a result of the degasification of coal and as a result of chemical reactions described below with the following equations:





Therefore, the system consists only of the following atoms: carbon, hydrogen, oxygen, nitrogen. Based on Dalton's law, the balancing elements of gasification process and equilibrium constants of the reactions, the following equations have been written for the system being in the equilibrium state:

$$p_{\text{CO}_2} + p_{\text{CO}} + p_{\text{H}_2} + p_{\text{CH}_4} + p_{\text{N}_2} + p_{\text{H}_2\text{O}} - 1 = 0 \quad (28)$$

$$(C) - (n_{\text{pal}}(C)_{\text{pal}} + n_{\text{kon}}(C)_{\text{kon}}) = 0 \quad (29)$$

$$(H) - (n_{\text{pal}}(H)_{\text{pal}} + n_{\text{kon}}(H)_{\text{kon}}) = 0 \quad (30)$$

$$(O) - (n_{\text{pal}}(O)_{\text{pal}} + n_{\text{pal}}(O)_{\text{kon}}) = 0 \quad (31)$$

$$(N) - (n_{\text{pal}}(N)_{\text{pal}} + n_{\text{kon}}(N)_{\text{kon}}) = 0 \quad (32)$$

$$K_1 = \frac{p_{\text{CO}}^2}{p_{\text{CO}_2}} \quad (33)$$

$$K_2 = \frac{p_{\text{CO}} p_{\text{H}_2}}{p_{\text{H}_2\text{O}}} \quad (34)$$

$$K_3 = \frac{p_{\text{CH}_4}}{p_{\text{H}_2}^2} \quad (35)$$

where:

$(C)_{\text{pal}}, (H)_{\text{pal}}, (O)_{\text{pal}}, (N)_{\text{pal}}$ – the number of particular elements in the fuel (kmole of element / kmole of fuel)

$(C)_{\text{kon}}, (H)_{\text{kon}}, (O)_{\text{kon}}, (N)_{\text{kon}}$ – the number of particular elements in the conversion agent (kmole of element / kmole of conversion agent)

$(C), (H), (O), (N)$ – the number of particular elements in the resultant gas formed after the gasification of n_{pal} kmols of fuel with n_{kon} kmols of conversion agent (kmole of element)

$p_{\text{CO}_2}, p_{\text{CO}}, p_{\text{H}_2}, p_{\text{CH}_4}, p_{\text{N}_2}, p_{\text{H}_2\text{O}}$ – partial pressure of, respectively, carbon dioxide, carbon monoxide, hydrogen, methane, nitrogen, steam, in atm

$n_{\text{pal}}, n_{\text{kon}}$ – the amount of fuel and conversion agent reacting with each other, kmole

K_1, K_2, K_3 – equilibrium constants of the chemical reactions

What is more, there is also a relationship between the partial pressure of particular gases and the balance of elements in the resultant gas. If it is assumed that the resultant gas consists only of such substances as: carbon dioxide, carbon monoxide, nitrogen, methane, hydrogen, steam, the above-mentioned relations can be written as follows:

$$\frac{(C)}{n} p = p_{\text{CO}_2} + p_{\text{CO}} + p_{\text{CH}_4} \quad (36)$$

$$\frac{(H)}{n} p = 2p_{\text{H}_2\text{O}} + 2p_{\text{H}_2} + 4p_{\text{CH}_4} \quad (37)$$

$$\frac{(O)}{n} p = 2p_{\text{CO}_2} + p_{\text{CO}} + p_{\text{H}_2\text{O}} \quad (38)$$

$$\frac{(N)}{n} p = 2p_{\text{N}_2} \quad (39)$$

where:

n – number of kmols of the resultant gas, kmole

p – pressure of the process, atm

Assuming that the process is carried out at the atmospheric pressure and one kmole of the resultant gas is produced, the equations (36)–(39) are simplified to the following form:

$$(C) = p_{\text{CO}_2} + p_{\text{CO}} + p_{\text{CH}_4} \quad (40)$$

$$(H) = 2p_{\text{H}_2\text{O}} + 2p_{\text{H}_2} + 4p_{\text{CH}_4} \quad (41)$$

$$(O) = 2p_{\text{CO}_2} + p_{\text{CO}} + p_{\text{H}_2\text{O}} \quad (42)$$

$$(N) = 2p_{\text{N}_2} \quad (43)$$

The following set of equations with eight unknowns is the result of combination of the equations (28)–(35) and (40)–(43):

$$p_{\text{CO}_2} + p_{\text{CO}} + p_{\text{H}_2} + p_{\text{CH}_4} + p_{\text{N}_2} + p_{\text{H}_2\text{O}} - 1 = 0$$

$$n_{\text{pal}}(H)_{\text{pal}} + n_{\text{kon}}(H)_{\text{kon}} = 2p_{\text{H}_2\text{O}} + 2p_{\text{H}_2} + 4p_{\text{CH}_4}$$

$$n_{\text{pal}}(C)_{\text{pal}} + n_{\text{kon}}(C)_{\text{kon}} = p_{\text{CO}_2} + p_{\text{CO}} + p_{\text{CH}_4}$$

$$n_{\text{pal}}(O)_{\text{pal}} + n_{\text{kon}}(O)_{\text{kon}} = 2p_{\text{CO}_2} + p_{\text{CO}} + p_{\text{H}_2\text{O}}$$

$$n_{\text{pal}}(N)_{\text{pal}} + n_{\text{kon}}(N)_{\text{kon}} = 2p_{\text{N}_2}$$

$$K_1 = \frac{p_{\text{CO}}^2}{p_{\text{CO}_2}} \quad (44)$$

$$K_2 = \frac{p_{\text{CO}} p_{\text{H}_2}}{p_{\text{H}_2\text{O}}}$$

$$K_3 = \frac{p_{\text{CH}_4}}{p_{\text{H}_2}^2}$$

The input data consists of the coal sample composition (in terms of the mass fractions of carbon, hydrogen, oxygen, elemental nitrogen and moisture), composition of the conversion agent as well as the temperature and pressure of the process.

The partial pressure of particular gases, the number of moles of the fuel and the gasifying agent constitute the solution of the set of equations. Due to the fact that the calculations are made for the atmospheric pressure and with the assumption that 1 kmole of the resultant gas is produced, the partial pressure of gases is equal to the molar fraction (volume fraction) and the number of moles of particular gases in the mixture.

$$p_i = x_i = \frac{n_i}{n} \quad (45)$$

where:

p_i – partial pressure i -th component of the mixture, atm

x_i – molar fraction of i -th composition in the mixture

n_i – number of kmols of particular gases, kmole

5. EXPERIMENT OF STEAM GASIFICATION OF COAL

The results of experiments concerning coal steam gasification carried out in laboratory conditions were presented in earlier works (Smoliński 2008, 2011). The experiments were conducted in a laboratory installation consisting of a fixed-bed reactor, resistance furnace, water pump with steam generator, water trap, mass-flow meter and gas chromatograph. The coal sample (3.1 g) was placed at the bottom of the reactor and heated to a temperature of 973 K under an inert gas (nitrogen) atmosphere. During the operations of the reactor, the pressure and temperature inside the reactor were controlled. After the temperature had stabilized, steam was injected to the reactor at a flow rate of $5.33 \cdot 10^{-2} \text{ cm}^3/\text{s}$. The synthesis gas was transported to the water-cooled tar trap. Flow-metre and gas microchromatograph automatically measured the composition of gas mixture every 192 seconds.

The physiochemical parameters of coal and the composition of the received gas are presented respectively in Tables 1 and 2. The average composition of the synthesis gas was calculated as the arithmetic mean of results from particular time periods (rejecting the initial and final results).

6. EQUILIBRIUM MODEL OF COAL GASIFICATION PROCESS

In the first stage, the concept model of the described experiments was shown in Figure 1. Steam (gasifying agent) and energy in the form of heat (it was assumed that the system temperature is constant and equals to 973 K) are supplied to the system. The coal sample with the parameters specified in Table 1 is placed to the system. It was assumed that the flow of the agent is so slow that a pseudo-equilibrium state is determined. It was considered that heterogeneous reactions take place in the system, as a result of which, a gas mixture is produced: carbon dioxide, carbon monoxide, methane, hydrogen, steam, nitrogen.

The content of particular elements in the fuel and gasifying agent was calculated according to the equations (13)–(16), (18) and (19). The results of these calculations are presented in Table 3. The gasifying agent is composed solely of hydrogen and oxygen atoms. The following elements were taken into consideration in the composition of coal: carbon, hydrogen, oxygen, nitrogen.

The equilibrium constants at a temperature of $T = 973 \text{ K}$ were calculated according to the approximate equations proposed by Gumz and based on data of the Bureau of Standards (Kozaczka 1994):

$$\log K_1 = 3,2673 - 8820,69 T^{-1} - 1,208714 \cdot 10^{-3} T + 0,153734 \cdot 10^{-6} T^2 + 2,295483 \log T \quad (46)$$

$$\log K_2 = 0,8255488 \cdot 10^{-6} T^2 + 14,51576 \log T - 4825,986 T^{-1} - 5,671122 \cdot 10^{-3} T - 33,45778 \quad (47)$$

$$\log K_3 = 4662,8 T^{-1} - 2,09594 \cdot 10^{-3} T + 0,3863 \cdot 10^{-6} T^2 + 3,034338 \log T - 13,06361 \quad (48)$$

Table 1. Physicochemical parameters of coal (Smoliński 2008)

Sample no.	Weight fraction								Heat of combustion, kJ/kg	Sintering point °C	Softening point °C	Melting point, °C	Flow temperature, °C
	moisture (W)	dust (A)	sulphur (S)	carbon (C)	hydrogen (H)	nitrogen (N)	oxygen* (O)	volatile matter (V)					
1	0.1105	0.1040	0.0185	0.6047	0.0346	0.0054	0.1277	0.3182	24 515	1 010	1 390	1 500	1 500
2	0.0916	0.0835	0.0088	0.6420	0.0393	0.0076	0.1348	0.2977	26 218	970	1 290	1 340	1 370
3	0.0744	0.0720	0.0192	0.6736	0.0414	0.0092	0.1194	0.3237	27 815	940	1 280	1 360	1 430
4	0.0164	0.1017	0.0131	0.7505	0.0428	0.0109	0.0755	0.3024	30 654	1 030	1 360	1 500	1 500
5	0.0446	0.1143	0.0160	0.6328	0.0428	0.0093	0.1495	0.3435	25 943	950	1 350	1 480	1 500
6	0.0602	0.0569	0.0050	0.7064	0.0408	0.0098	0.1307	0.3112	28 805	990	1 270	1 350	1 370
7	0.0493	0.0565	0.0065	0.7272	0.0432	0.0104	0.1173	0.3584	29 529	1 000	1 370	1 410	1 430
8	0.0915	0.0893	0.0071	0.6372	0.0382	0.0067	0.1367	0.3049	25 855	950	1 220	1 260	1 300
9	0.0650	0.2873	0.0082	0.4962	0.0346	0.0089	0.1087	0.2529	20 043	980	1 360	1 500	1 500
10	0.1106	0.0696	0.0203	0.6262	0.0330	0.0088	0.1349	0.2044	25 336	990	1 270	1 350	1 420
11	0.0136	0.0715	0.0030	0.7975	0.0442	0.0135	0.0702	0.2880	32 743	970	1 310	1 340	1 370

* The oxygen content was calculated from the formula $O = 1 - (W + A + C + H + S)$.

Table 2. Molar fraction (average, maximum, minimum) of particular gases in the mixture, result of the experiment (Smoliński 2008)

Sample no.	Molar fraction of gases in mixture											
	X_{CO_2}			X_{CO}			X_{CH_4}			X_{H_2}		
	average	min.	max.	average	min.	max.	average	min.	max.	average	min.	max.
1	0.2649	0.2584	0.2741	0.0971	0.0781	0.1207	0.0093	0.0055	0.0130	0.6288	0.6077	0.6488
2	0.3304	0.3170	0.3535	0.0343	0.0093	0.0474	0.0000	0.0000	0.0000	0.6353	0.6229	0.6441
3	0.2180	0.1978	0.2300	0.1471	0.0867	0.2159	0.0025	0.0000	0.0078	0.6324	0.5863	0.6856
4	0.2387	0.2300	0.2482	0.1413	0.1268	0.1545	0.0276	0.0235	0.0310	0.5924	0.5722	0.6187
5	0.3389	0.3106	0.3667	0.0359	0.0209	0.0719	0.0000	0.0000	0.0000	0.6253	0.6124	0.6447
6	0.2437	0.2215	0.2558	0.1473	0.1303	0.1927	0.0109	0.0100	0.0130	0.5981	0.5729	0.6115
7	0.2548	0.2363	0.2845	0.1234	0.1026	0.1428	0.0207	0.0000	0.0255	0.6012	0.5831	0.6319
8	0.2780	0.2627	0.2880	0.0911	0.0816	0.1210	0.0082	0.0069	0.0117	0.6226	0.6045	0.6346
9	0.1791	0.1676	0.2085	0.2060	0.1756	0.2305	0.0000	0.0000	0.0000	0.6149	0.6019	0.6334
10	0.2586	0.2479	0.2632	0.1135	0.1084	0.1191	0.0160	0.0127	0.0787	0.6119	0.6035	0.6290
11	0.2040	0.1847	0.2218	0.2267	0.1847	0.2521	0.0139	0.0113	0.0161	0.5554	0.5100	0.6152

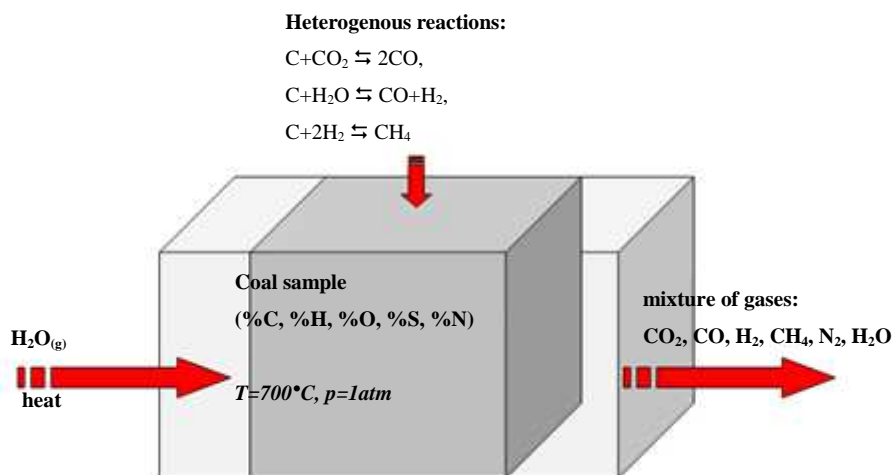


Fig. 1. Model of steam gasification of coal – I stage

Table 3. The content of elements in the fuel and gasifying agent

Sample no.	Content of elements					
	in fuel, kmole/kmole of fuel				in gasifying agent, kmole/kmole of gasifying agent	
	(C) _{pal}	(H) _{pal}	(O) _{pal}	(N) _{pal}	(H) _{kon}	(O) _{kon}
1	0.6412	0.5965	0.1797	0.0049	2	1
2	0.6446	0.5961	0.1628	0.0065	2	1
3	0.6555	0.5800	0.1354	0.0077	2	1
4	0.7106	0.5070	0.0640	0.0088	2	1
5	0.6422	0.5816	0.1440	0.0081	2	1
6	0.6751	0.5446	0.1320	0.0080	2	1
7	0.6795	0.5458	0.1129	0.0083	2	1
8	0.6474	0.5897	0.1662	0.0058	2	1
9	0.6243	0.6315	0.1571	0.4012	2	1
10	0.6499	0.5715	0.1853	0.0078	2	1
11	0.7218	0.4965	0.0559	0.0102	2	1

The set of equations (44) was solved numerically in Mathematica software, using the FindRoot procedure (Grzymkowski et al. 2008). The final results of the calculations are presented in Table 4.

Table 4. Calculated molar fraction of particular gases in the mixture, the result of modelling – I stage

Sample no.	Molar fraction of gases in mixture					
	X _{CO2}	X _{CO}	X _{CH4}	X _{H2}	X _{H2O}	X _{N2}
1	0.0831	0.2985	0.0127	0.5121	0.0920	0.0015
2	0.0807	0.2941	0.0048	0.5255	0.0930	0.0019
3	0.0793	0.2917	0.0053	0.5286	0.0928	0.0022
4	0.0799	0.2928	0.0235	0.5113	0.0901	0.0025
5	0.0798	0.2926	0.0062	0.5264	0.0927	0.0024
6	0.0817	0.2960	0.0123	0.5158	0.0919	0.0023
7	0.0829	0.2947	0.0182	0.5128	0.0909	0.0024
8	0.0813	0.2954	0.0054	0.5232	0.0923	0.0017
9	0.0782	0.2896	0.0036	0.5329	0.0929	0.0029
10	0.0834	0.3000	0.0071	0.5139	0.0928	0.0024
11	0.0787	0.2905	0.0131	0.5236	0.0915	0.0027

The calculations made give acceptable results (co-ordinal) with respect to the content of hydrogen and methane in the synthesis gas (Tab. 2 and 4). The calculated content of carbon monoxide and carbon dioxide in the synthesis gas differs by one order of magnitude from the experimental results. The

calculated CO content is too high and the CO₂ content – too low in comparison to the results of the experiment. A possible reason for the discrepancies is presented below.

The calculation algorithm should be complemented by a reaction which changes (decreases) the concentration of CO in the resultant gas. An exothermic water gas shift reaction complies with it. The equilibrium of the reaction at a temperature of 973 K is shifted towards the formation of H₂ and CO₂ – the equilibrium constant is 1.55.

What is more, the reaction of methane formation does not actually reach the state described by the equation (35). For a closer characterization of this reaction to the actual conditions, an empirical factor correcting the numerical value of the equilibrium constant K_3 is applied. The value of this factor depends on the type of coal (Kozaczka 1994). Thus, based on the literature prerequisites, a multiplier of the equilibrium constant of methane synthesis reaction was used. According to Kozaczka (1994), this multiplier may be set between 0.115–0.570, depending on the type of coal. In this thesis, the value of the factor was chosen in such a way as to simultaneously meet the requirements described by the following formulas:

$$(\tilde{x}_{CH_4} - x_{CH_4})^2 = \min \quad (49)$$

$$0,1 \leq \kappa_3 \leq 1 \quad (50)$$

where:

\tilde{x}_{CH_4} , x_{CH_4} – molar fraction of methane in the resultant gas, respectively the experimental data and results of calculations

κ_3 – multiplier of the equilibrium constant of methane synthesis reaction

Table 5 contains the calculated values of correction factors for each of the samples separately. Based on the above calculations, a hypothesis concerning the existence of the relationship between the content of elemental carbon in the sample and the value of the correction factor κ_3 was formulated. The equation approximating the value of the factor κ_3 takes the following form:

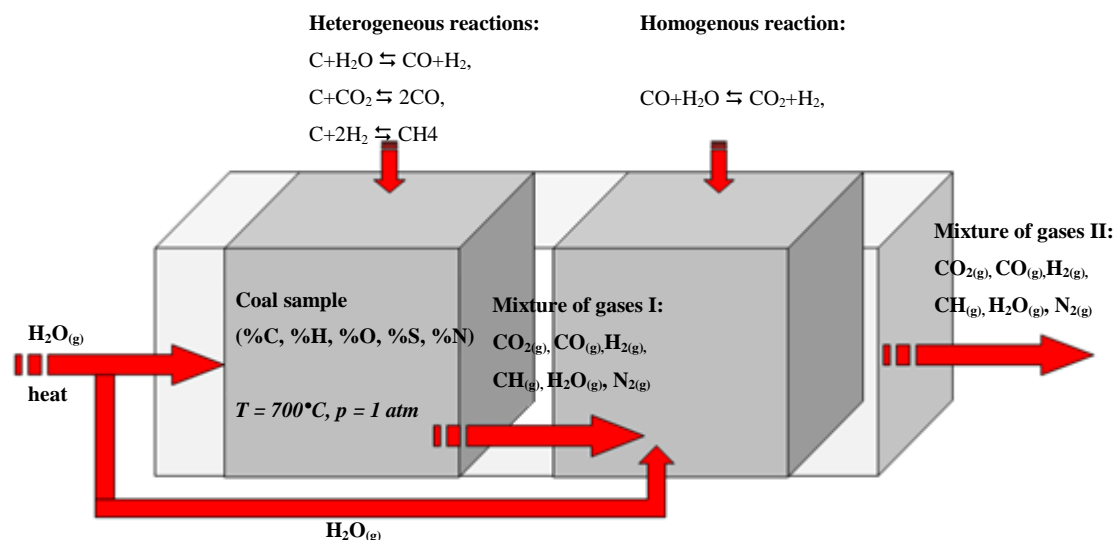
$$\kappa_3 = -4\,448,641\,C^4 + 11\,635,115\,C^3 - 11\,304,516\,C^2 + 4\,833,906\,C - 766,946 \quad (51)$$

where C – the mass fraction of elemental carbon in the sample, $C \in (0.49-0.80)$

Table 5. Factors correcting the numerical value of the equilibrium constant of methane synthesis reaction [determined on the basis of experimental data (Smoliński 2008)]

Sample no.	$K_{3,i}$
1	0.238
2	0.100
3	0.100
4	0.730
5	0.100
6	0.277
7	0.541
8	0.207
9	0.100
10	0.430
11	0.346

The above assumptions allow the concept of two-zone reactor (Fig. 2) to be adapted. For the first zone of the reactor, the model of the phenomenon is analogous to the one-zone reactor, however the set of equations (44) was modified in the computation scheme – the corrected value $\kappa_3 K_3$ was inserted in the place of K_3 . The gas mixture from the first zone as well as the part of steam which was introduced to the system but which did not react in the first zone (hereinafter: excess amount of steam), were entered into the second zone. A conversion reaction of carbon monoxide with steam takes place and a new equilibrium state is determined.

**Fig. 2.** Model of steam gasification of coal – II stage

The reactivity of coal in the gasification process determines the rate of coal reaction with the gasifying agent and it determines that various amounts of gases are produced in a particular time interval from various samples. The coal reactivity depends on many factors, among which the most important are: content of elemental carbon, volatile matter and ash (Smoliński, Howaniec 2007). Therefore, a hypothesis that it is possible to approximate the excess amount of steam with the equation including those parameters was formulate

$$n_{\text{H}_2\text{O}, \text{nad}} = \sum_{i=0} \sum_{j=0} \sum_{k=0} b_{ijk} C^i A^j V^k \quad (52)$$

where:

$n_{\text{H}_2\text{O}, \text{nad}}$ – excess amount of steam supplied to the second zone of the system, kmole

C, A, V – mass fraction in the sample of respectively: carbon, ash, volatile matter

b_{ij} – parameters of adjusting the polynomial, kmole

The above-specified polynomial is only an example of the description concerning the relationship between the composition of coal and the amount of steam supplied to the second zone of the reactor. The development of a complete model requires more experimental data. Moreover, an accurate measurement of the amount of gasifying agent (steam) supplied to the system and remaining in the resultant mixture after it leaves the system is necessary for the assumed calculation scheme. At this stage of the thesis, the optimal excess

amount of water vapour $n_{\text{H}_2\text{O}, \text{nad}}$ was calculated on the basis of the experimental data, according to the below assumption:

$$(\tilde{x}_{\text{CO}_2} - x'_{\text{CO}_2})^2 + (\tilde{x}_{\text{CO}} - x'_{\text{CO}})^2 + (\tilde{x}_{\text{H}_2} - x'_{\text{H}_2})^2 = \min \quad (53)$$

where:

\tilde{x}_i – molar fraction of particular gases in the mixture (experimental data)

x'_i – molar fraction of particular gases in the mixture (model).

The results of the calculations are presented in Table 6.

Table 6. Estimated optimal excess amount of steam in the II zone of the reactor

Sample no.	$n_{\text{H}_2\text{O}, \text{nad}}$, kmole
1	1.697
2	6.443
3	0.659
4	0.719
5	4.972
6	0.748
7	0.932
8	1.706
9	0.322
10	1.156
11	0.251

The following equation was written down and it constitutes the basis for the calculation of a new equilibrium state

$$K_4 = \frac{(n_{\text{CO}_2} + y) \cdot (n_{\text{H}_2} + y)}{(n_{\text{CO}} - y) \cdot (n_{\text{H}_2\text{O}} + n_{\text{H}_2\text{O,nad}} - y)} \quad (54)$$

where:

$n_{\text{CO}_2}, n_{\text{CO}}, n_{\text{H}_2}, n_{\text{H}_2\text{O}}$ – the amount of, respectively: carbon dioxide, carbon monoxide, hydrogen, steam in the mixture received in the first zone of the reactor, kmole

$$\log K_4 = 36,72508 - 3994,704 T^{-1} + 4,462408 \cdot 10^{-3} T - 0,671814 \cdot 10^{-6} T^2 - 12,220277 \log T \quad (55)$$

The parameter y was determined from the equation (54). The molar fraction of particular gases in the mixture in the newly established equilibrium state was calculated using the following equations:

$$x_{\text{CO}_2} = \frac{n_{\text{CO}_2} + y}{n} \quad (56)$$

$$x_{\text{CO}} = \frac{n_{\text{CO}} - y}{n} \quad (57)$$

$$x_{\text{CH}_4} = \frac{n_{\text{CH}_4}}{n} \quad (58)$$

$$x_{\text{H}_2} = \frac{n_{\text{H}_2} + y}{n} \quad (59)$$

$$x_{\text{H}_2\text{O}} = \frac{n_{\text{H}_2\text{O}} + n_{\text{H}_2\text{O,nad}} - y}{n} \quad (60)$$

$$x_{\text{N}_2} = \frac{n_{\text{N}_2}}{n} \quad (61)$$

$$n = n_{\text{CO}_2} + n_{\text{CO}} + n_{\text{CH}_4} + n_{\text{H}_2} + n_{\text{H}_2\text{O}} + n_{\text{H}_2\text{O,nad}} + n_{\text{N}_2} \quad (62)$$

The results of the experiment refer to the content of such gases as: carbon dioxide, carbon monoxide, methane, hydrogen, thus the molar composition of the mixture was calculated into those components according to the following formulas:

$$x'_{\text{CO}_2} = \frac{x_{\text{CO}_2}}{(1 - x_{\text{H}_2\text{O}} - x_{\text{N}_2})} \quad (63)$$

$$x'_{\text{CO}} = \frac{x_{\text{CO}}}{(1 - x_{\text{H}_2\text{O}} - x_{\text{N}_2})} \quad (64)$$

$$x'_{\text{CH}_4} = \frac{x_{\text{CH}_4}}{(1 - x_{\text{H}_2\text{O}} - x_{\text{N}_2})} \quad (65)$$

$$x'_{\text{H}_2} = \frac{x_{\text{H}_2}}{(1 - x_{\text{H}_2\text{O}} - x_{\text{N}_2})} \quad (66)$$

The calculated content of gases in the mixture remains in good correlation with the results of the experiment. The results of the calculations are presented in Table 7.

$n_{\text{H}_2\text{O,nad}}$ – excess amount of water vapour (supplied to the second zone of the reactor), kmole

y – the amount of carbon dioxide produced in the conversion reaction of carbon monoxide with steam, kmole

K_4 – equilibrium constant of the conversion reaction of carbon monoxide with steam

The equilibrium constant at temperature of $T = 973$ K was calculated according to the approximating equation proposed by Gumz (Kozaczka 1994).

Table 7. Comparison of the composition of synthesis gas calculated in accordance with the equilibrium method with experimental data (Smoliński 2008)

Sample no.	Data	Molar fraction of gases in mixture				Correlation factor
		x_{CO_2}	x_{CO}	x_{CH_4}	x_{H_2}	
1	experiment	0.2649	0.0971	0.0093	0.6288	0.99
	model	0.2634	0.0780	0.0114	0.6472	
2	experiment	0.3304	0.0343	0.0000	0.6353	0.99
	model	0.2960	0.0241	0.0041	0.6758	
3	experiment	0.2180	0.1471	0.0025	0.6324	1.00
	model	0.2089	0.1467	0.0051	0.6393	
4	experiment	0.2387	0.1413	0.0276	0.5924	1.00
	model	0.2152	0.1382	0.0223	0.6243	
5	experiment	0.3389	0.0359	0.0000	0.6253	0.99
	model	0.2899	0.0305	0.0053	0.6743	
6	experiment	0.2437	0.1473	0.0109	0.5981	1.00
	model	0.2200	0.1374	0.0116	0.6309	
7	experiment	0.2548	0.1234	0.0207	0.6012	1.00
	model	0.2312	0.1186	0.0170	0.6333	
8	experiment	0.2780	0.0911	0.0082	0.6226	1.00
	model	0.2606	0.0775	0.0048	0.6571	
9	experiment	0.1791	0.2060	0.0000	0.6149	1.00
	model	0.1669	0.2040	0.0037	0.6255	
10	experiment	0.2586	0.1135	0.0160	0.6119	1.00
	model	0.2471	0.1049	0.0065	0.6415	
11	experiment	0.2040	0.2267	0.0139	0.5554	0.98
	model	0.1551	0.2219	0.0133	0.6096	

7. SUMMARY

It was shown in the thesis that the equilibrium model is adequate for the estimation of the gas composition obtaining from the steam gasification of coal in the fixed-bed reactor.

A concept concerning the division of a model reaction system into two zones was developed. It was assumed that the gas mixture which was produced in the first zone and the part of steam which was supplied to the system but did not react in the first zone, were entered to the second zone of the reactor. Due to the lack of sufficient experimental data at this stage of work, the optimum amount of unreacted steam was estimated based on the experimental data. It was found that an accurate measurement of the gasifying agent amount (steam) supplied to the system and remaining in the resultant mixture after leaving the system, is necessary for the assumed calculation scheme. The calculated content of gases in the mixture remains in good correlation with the results of the experiment.

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